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**DEPARTMENT OF CHEMISTRY
JOHN SCHOFF MILLIS SCIENCE CENTER
CASE WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO 44106**

TECHNICAL REPORT NO. 45

**SPECULAR REFLECTANCE STUDIES
OF BROMIDE ADSORPTION
ON GOLD**

BY

Radoslav Adžić, Ernest Yeager and B. D. Cahan

1 December 1976

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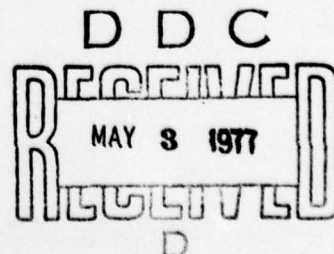
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1 December 1976

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Various mechanisms for the substantial changes in reflectance attending the specific adsorption of anions are discussed. The observed effects cannot be explained on the basis of changes in the charge on the electrode and corresponding changes in the contribution of the conduction band to the surface optical properties. The principal mechanism is proposed to be modifications in the surface electronic states of the metal electrode through direct orbital interactions between the adsorbed anions and the metal.

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SPECULAR REFLECTANCE STUDIES OF BROMIDE ADSORPTION ON GOLD^{*}

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ABSTRACT

Specular reflectance changes have been used to examine the specific adsorption of bromide on gold in the presence of a large excess of supporting electrolyte (NaF) which is not specifically adsorbed. A linear relation has been demonstrated between the reflectance changes and the surface excess of bromide through the examination of the time dependence of the reflectance under conditions where the rate of adsorption of the bromide is diffusion controlled and hence known. The adsorption isotherms have been found to follow Temkin behavior. The electrosorption valency has been evaluated from the charge and surface excess at constant potential and found to be -0.49 to -0.59, depending on the potential.

Various mechanisms for the substantial changes in reflectance attending the specific adsorption of anions are discussed. The observed effects cannot be explained on the basis of changes in the charge on the electrode and corresponding changes in the contribution of the conduction band to the surface optical properties. The principal mechanism is proposed to be modifications in the surface electronic states of the metal electrode through direct orbital interactions between the adsorbed anions and the metal.

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INTRODUCTION

The adsorption of ions on electrode surface is attended by substantial changes in the specular reflectivity (1) and the ellipsometric parameters (2). These changes can be used to determine the adsorption isotherms provided the reflectance changes can be shown to be directly a measure of the concentration of these ions in the double layer. In most prior reflectivity studies of ionic adsorption, insufficient evidence for such a direct relation has been presented.

The purpose of the present paper is to present such evidence for bromide adsorption on gold electrodes and to use the reflectance changes to evaluate the adsorption isotherms. For a summary of prior studies of ionic adsorption using specular reflectance and ellipsometry, the reader is referred to the reviews of McIntyre (3) and Blondeau and Yeager (4).

BACKGROUND

Consider the addition of a specifically adsorbed ion to a solution containing a non-specifically adsorbed supporting electrolyte with the potential of the working electrode held constant relative to an invariant reference electrode. The change in reflectance may be divided into three contributions; i.e.

$$\Delta R = \Delta R_1 + \Delta R_2 + \Delta R_3 \quad (1)$$

where ΔR_1 arises from the ionic specific adsorption, ΔR_2 is caused by changes in the remainder of the ionic double layer and ΔR_3 from the refractive index change of the bulk solution. The first term is of principal interest since it carries the information concerning specific adsorption. The last term ΔR_3 is very small and can be eliminated from the measurements by the optical procedure described later. This then leaves the question of the relative importance of the ΔR_2 term.

In most instances, the intrinsic optical changes in the outer Helmholtz plane and diffuse double layer are expected (5) to have only a small effect on the reflectance and ΔR_2 will be associated with the changes in the charge on the electrode dq_m ; i.e.,

$$-dq_m = dq_{dl} = dq'_{dl} + (z + \lambda)(n_s) d\theta \quad (2)$$

where dq_{dl} is the differential change in the total double layer charge, dq'_{dl} is the corresponding change excluding the inner Helmholtz plane, n_s is the saturation surface concentration of the specifically adsorbed ion, θ is its fractional coverage and z and λ are defined by



where λ corresponds to the electronic charge transferred across the interface from the metal to the adsorbed species and cannot be directly determined. The differential charge provided through the external circuit dq'_m is related to dq_m through the equations:

$$dq'_m = dq_m + \lambda F n_s d\theta \quad (4)$$

$$= -dq'_{dl} - z F n_s d\theta \quad (5)$$

The specifically adsorbed ions in the inner Helmholtz plane can produce the change ΔR_1 not only by changes in the charge on the metal q_m but also by direct orbital interactions with the electrode surface. The intrinsic optical properties of the inner Helmholtz layer also are modified although this contribution to ΔR_1 is usually smaller than those just cited - particularly if the light is parallel polarized and near the pseudo Brewster angle ($\sim 45^\circ$) for this plane.

On the basis of these considerations, the differential reflectance changes can be expressed as:

$$\left(\frac{dR}{R}\right)_E = \frac{1}{R} \left[\left(\frac{\partial R}{\partial \theta}\right)_{E,q'} d\theta + \left(\frac{\partial R}{\partial q'}\right)_{dl} dq'_{dl} \right]_E \quad (6)$$

where ΔR_3 in eq. 1 has been omitted. To use reflectance changes to evaluate θ without complications requires that the reflectance changes be proportional to θ . Inspection of eq. 6 indicates that this requires $\left(\frac{\partial R}{\partial \theta}\right)_{E,q'}$ to be independent of θ and the second bracketed term to be either very small compared to the first or for the changes in q'_{dl} to be directly proportional to the changes in θ .

EXPERIMENTAL APPROACH

The specular reflectance of the gold electrodes has been followed during linear sweep voltammetry with and without Br^- in 0.8 M NaF as a supporting electrolyte. The change in relative reflectance $(\Delta R/R)_E$ produced by the addition of the bromide has then been calculated from these data for a given potential E from the expression

$$\left(\frac{\Delta R}{R_o}\right)_E = \left(\frac{R_E - R_o}{R_o}\right)_C - \left(\frac{R_E - R_o}{R_o}\right)_{C=0} \quad (7)$$

where C is the bulk concentration of the halide ions and R_o is measured at a negative potential where halide adsorption is expected to be negligible. This arrangement cancels out ΔR_3 and also eliminates any error associated with duplicating absolute reflectivities from run to run.

The changes in charge produced by Br^- ions at a given potential have been determined by integrating the voltammetry curves from negative potentials where Br^- specific adsorption should be negligible to the particular potential with and without Br^- ions present. Evidence that the reflectance changes are directly proportional to the specifically adsorbed halide in the presence of a supporting electrolyte has been obtained by measuring the dependence of the reflectivity on the total surface excess of bromide Γ at constant potential. The surface excess has been determined by stepping the potential from a value at which specific adsorption is negligible to a value at which specific adsorption occurs under conditions where the adsorption of halide is under pure diffusion control. The values of Γ then have been calculated from the diffusion coefficient and bulk Br^- concentration using the Sand equation.

EXPERIMENTAL DETAILS

The cylindrical optical electrochemical cell and associated optical system have been described elsewhere (6,7). All reflectance measurements were made with parallel polarization at an angle of incidence of 45° . The intensity of the reflected light was measured with a Hamamatsu R-37⁴ photomultiplier with the d.c. signal amplified and measured directly on an X-Y recorder during the linear potential sweeps and also following the potential step in the experiments directed at establishing the relationship between $\Delta R/R_0$ and Γ . A Wenking potentiostat was used to control the potentials.

The solutions involved 0.8 M NaF as the supporting electrolyte with small additions of NaBr. The pH of the solutions was adjusted to 9 through

the addition of small quantities of purified carbonate free NaOH. The solutions were prepared from Alfa Inorganics ultra pure NaF together with triply distilled water.

The working electrodes were bulk gold plates of 99.99% purity. The electrodes were polished first with abrasive papers and finally with alumina powders of decreasing particle size 0.5 μ down to 0.06 μ . After polishing, the electrodes were washed with 10 μ KOH and concentrated HNO_3 and then rinsed and stored in triply distilled water.

The counter electrode consisted of a hydrogen-saturated palladium plate, mounted parallel to the working electrode at a distance of 2 cm, just outside the optical path. The reference electrode (RE) was an α -PdH bead of 1 mm diameter mounted on the end of a fine glass tube with the center of the bead located typically at a distance of 0.5 mm from the working electrode, outside of the optical path.

Nitrogen gas, purified by passing it over treated copper turnings and then through molecular sieves (Linde 4A and 13X), was bubbled through the solution before measurements to remove dissolved O_2 and a H_2 atmosphere maintained above the solution during the measurements. All measurements were carried out at room temperature (22° C).

RESULTS AND DISCUSSION

Effects of Br^- Adsorption on Reflectance

Figure 1 shows the effects of additions of varying amounts of Br^- on the reflectivity at 515 nm in 0.8 μ NaF with the solution adjusted to pH = 9.0. These curves were obtained by first adjusting the potential to

the most anodic value and maintaining it there for ∞ s to attain adsorption equilibrium. The potential was then swept in the cathodic direction at 10 mV/s. The reference potential for R_o in eq. 7 was -0.0 V vs RHE, which is sufficiently cathodic that no anions should be specifically adsorbed.

In Fig. 2 is a plot of the reflectance vs charge q'_m , obtained from integration of the voltammetry curve with and without Br^- . The large increment in slope attending the specific adsorption of bromide and the linearity provide evidence that the reflectivity changes are proportional to the amount of specifically adsorbed bromide. This plot also indicates that the reflectance changes attending the specific adsorption are not just a matter of the change in the charge on the metal Δq_m . Although Δq_m is not known, the charge supplied through the external circuit $\Delta q'_m$ during the specific adsorption of Br^- represents an upper limit for Δq_m since γ in eq. 4 should be positive. Thus the plots for $\Delta R/R$ vs q_m with and without Br^- present would not superimpose and, in fact, can only differ more.

Figure 3 indicates the time dependence of the reflectivity following the stepping of the electrode potential from 0.20 V to 0.70 V vs RHE. The linearity of the $\Delta R/R_o$ vs $t^{1/2}$ shows that the process is under diffusion control. This linearity also verifies that there is a direct proportion between $\Delta R/R_o$ at a given voltage and the total surface excess concentration of Br^- (Γ). With a large excess of a non-specifically adsorbed supporting electrolyte (0.8 M NaF), Γ consists almost entirely of the specifically adsorbed anion. Further, using the Sand equation, it is possible to calculate the values of Γ as a function of time and then to determine $(\Delta R/R_o / \partial \Gamma)_E$; i.e.,

$$(\partial \Gamma / \partial t)_E = C_O (D/\pi t)^{1/2} \quad (8)$$

$$\Gamma = 2 C_O (Dt/\pi)^{1/2} \quad (9)$$

and

$$\frac{1}{R_O} \left(\frac{\Delta R}{\Delta \Gamma} \right)_E = \frac{1}{2C_O} \left(\frac{\pi}{D} \right)^{1/2} \left(\frac{\partial R}{\partial t^{1/2}} \right)_E \quad (10)$$

This assumes that Br⁻ diffusion layer adjacent to the electrode does not have any significant direct optical effect on the reflectivity - a good assumption, particularly for parallel polarization at 45° (near the Brewster angle for such a layer). The right hand ordinate in Fig. 3 has been calculated using a value of $D = 2.08 \times 10^{-5} \text{ cm}^2/\text{s}$ (8) in eq. 9.

Adsorption Isotherms

Figure 4 shows the adsorption isotherms for bromide on Au at various potentials as obtained from the reflectivity measurements. The right hand ordinate indicates the values of Γ evaluated from $\Delta R/R_O$ using the value of $(1/R_O)(\Delta R/\Delta \Gamma)_E$ calculated with eq. 10 from the data in Fig. 3. The linearity of the $\Delta R/R_O$ or Γ vs $\log C_{\text{Br}^-}$ plots indicates that the adsorption of Br⁻ obeys the Temkin adsorption isotherm over a wide range of concentrations and potentials. No saturation coverage was found even at the most anodic potential involved in these experiments. The isotherms at various potentials have the same slope which means that the Temkin parameter is independent of potential.

The $\Delta R/R_O$ and Γ vs E plots are shown in Fig. 5 for several Br⁻ concentrations. The linearity is in agreement with Temkin behaviour. The dashed line corresponds to the Γ values for Br⁻ adsorption on Au by Paik et al. (9) using ellipsometric data. While their data also indicate Temkin

type behavior, the slope is quite different. This is not surprising since these workers calculated the equivalent of Γ from the optical properties of the double layer without considering the effects of the adsorbed ions on the surface optical properties of the metal side of the interface.

Electrosorption Valence

The electrosorption valence γ can be calculated from the Γ vs q'_m data in the presence of a supporting electrolyte with the expression

$$\gamma = - \frac{1}{F} \left(\frac{\partial q'_m}{\partial \Gamma} \right)_E \quad (11)$$

with the assumption that Γ is a good approximation for the surface concentration. Figure 6 presents plots of q'_m vs Γ for several voltages. The values of γ range from -0.49 for 0.5 V vs RHE to -0.59 for 0.7 V vs RHE. Taking into account the experimental scatter of the data, the electrosorption valence does appear to increase with electrode potential. The values of $\gamma \approx -0.5$ are larger than reported for Br^- on mercury (10), which suggests that the interaction of Br^- with Au is larger and involves a significant covalent bond contribution and not just ionic character.

The Temkin isotherm may be expressed in the form

$$n_{\text{Br}} = A(E) + (1/\rho) \ln C_{\text{Br}^-} \quad (11)$$

where the function $A(E)$ is given by

$$A(E) = A_0 + \left(\frac{F}{\rho RT} \right) E \quad (12)$$

according to Bagotzky et al. (11), and ρ is related to the Temkin parameter f'_\pm used by these authors by $f'_\pm = \rho / (n_{\text{Br}})_s$ where $(n_{\text{Br}})_s$ is the saturation coverage. Assuming $\Gamma = n_{\text{Br}}$ to be a good approximation, then

$$\left(\frac{\partial \ln C_{\text{Br}^-}}{\partial E} \right)_{\Gamma} \approx \left(\frac{\partial \ln C_{\text{Br}^-}}{\partial E} \right)_{n_{\text{Br}^-}} = \frac{F}{RT} \quad (13)$$

According to Schultze and Vetter (10), however,

$$\left(\frac{\ln C_{\text{Br}^-}}{\partial E} \right)_{\Gamma} = \gamma \frac{F}{RT} \quad (14)$$

where γ is the electroadsorption value for measurements carried out with a large excess of supporting electrolyte. The experimental value of $(\partial \log C_{\text{Br}^-} / \partial E)_{\Gamma}$ evaluated at $\Gamma = 0.6 \times 10^{-9}$ moles/cm² from Fig. 4 is 18 decades/V as compared with a value of 17 decades/V from eq. 13. Since γ is numerically much less than unity, the potential and concentration dependent terms in the experimental adsorption isotherm seem in conflict with the expected behavior taking into account the electroadsorption valency.

Determination of PZC

Takamura et al. (12) have suggested that the intersection of the two linear regions in the $\Delta R/R_0$ vs E curves may indicate the point of zero charge. They found the addition of iodide to a NaOH solution to shift this intersection by 60 mV/decade and interpreted this in terms of the Esin-Markov effect. Similar behavior has been found in the present study upon adding Br^- with NaF as the supporting electrolyte. The plot of this potential vs $\log C_{\text{Br}^-}$ in Fig. 7 indicates linear behavior over three decades with a slope of 57 mV/decade.

Difficulty has been encountered in finding literature values for E_{pzc} for Au under conditions comparable to those in the present study. For Au in 10^{-2} M NaBr + 0.8 M NaF, the reflectivity measurements indicate E_{pzc}

= -0.22 V vs SHE as compared with a value of -0.18 V vs SHE, for a 10^{-2} M NaBr solution reported by Bodé et al. (13). Further studies of the relation of reflectivity measurements to the pzc are needed before this approach can be considered fully confirmed.

Discussion of Mechanism For Reflectivity Changes Attending Ionic Specific Adsorption

The change of reflectivity produced by anion adsorption may involve contributions from various sources:

1. Changes in the charge on the metal q_m and hence changes in the contribution of the conduction band to surface optical properties as described in the treatments of e.g. McIntyre and Aspnes (14,15) and Garrigos et al. (16).
2. Changes in the surface plasmon contributions (4) arising from changes in the dielectric properties of the interface.
3. For metals involving interband transitions, changes in the electric field penetration into the metal and hence possible electroreflectance effects associated with the bending of the top of the valency band over distances into the metal of the order of the Thomas-Fermi screening distance (17,18).
4. Modifications in the surface electronic states of the metal electrode through direct orbital interactions between the adsorbed species and metal; i.e., bond formation. Electron transitions may also occur between these localized surface states and the conduction band as suggested by Cahan et al. (17).

5. Changes in the optical properties of the solution layer immediately adjacent to the electrode surface because of replacement of some solvent molecules by ions and modifications in the structure of this layer.

It is difficult to establish which of these mechanisms are predominant in the present reflectance-ionic adsorption studies. On the basis of the Stedman calculation (5), mechanism 5 appears unlikely in view of the experimental conditions (p-polarization, 45° angle of incidence) and the large magnitude of the effect. Mechanism 1 alone does not appear capable of explaining the observations discussed earlier in conjunction with Fig. 2. The image charges induced by specifically adsorbed ions, however, need to be taken into account, as pointed out by McIntyre and Peck (19), and might lead to enhancement of the charge modulation reflectivity coefficient $(1/R_o)(\partial R/\partial q_m)$.

The authors favor mechanism 4 as predominant but the evidence is weak. There is little question that the bonding of the Br to the surface has some covalent character. Such orbital interactions should produce relatively large changes in the optical constants of the surface. The even more pronounced reflectivity changes produced by I^- adsorption on Au (20) provide evidence that localized orbital interactions are important.

The dependence of the reflectance changes on type of adsorbed ion, wavelength and metal will help to resolve the question of mechanism. Some data of this kind are already available but more is needed. In the meantime, it is very important that electrochemists using reflectance and ellipsometric methods to evaluate the adsorption isotherms and kinetics demonstrate a linear relation between these optical quantities and the extent of adsorption. While linearity was found in the present study, this is not necessarily true in general.

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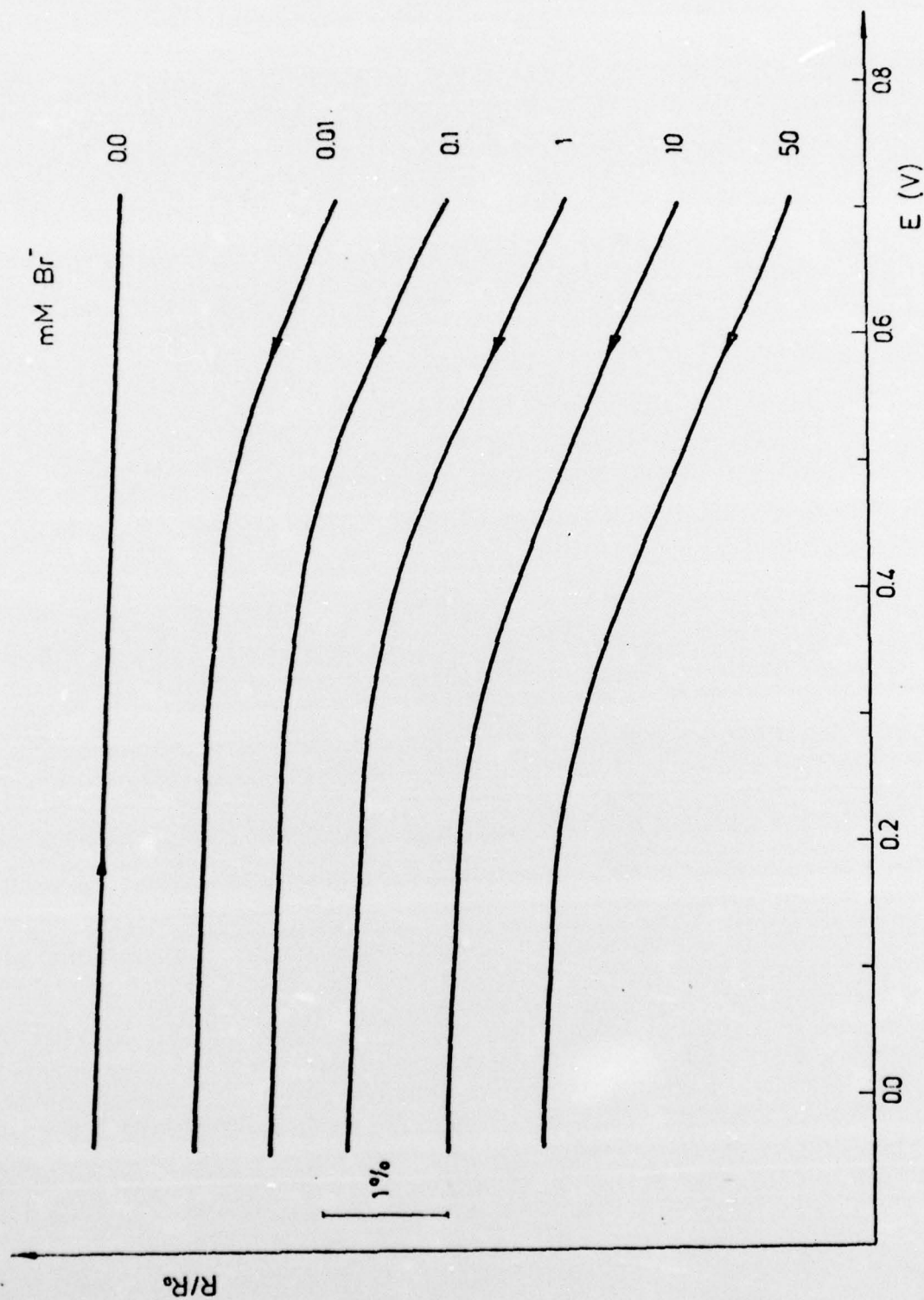


Fig. 1 Reflectivity-potential curves of gold in 0.8 M NaF, pH = 9.0 with various Br^- concentrations indicated in the curves. $\lambda = 500$ nm, parallel polarization, angle of incidence 45° . Voltage sweep: 10 mV/s, cathodic direction.

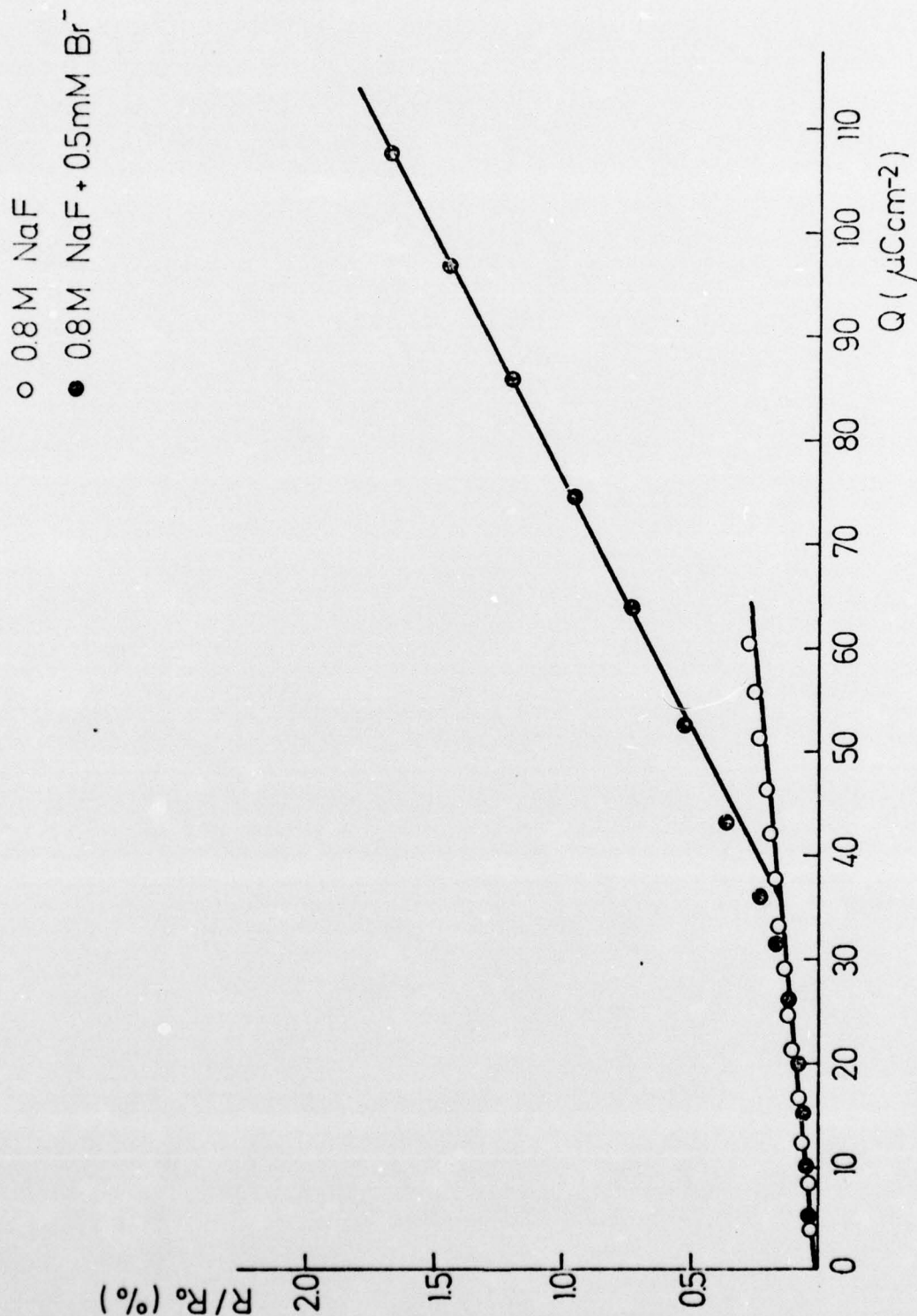


Fig. 2 Reflectivity-charge curves with (●) and without (○) Br⁻ present in 0.8 M NaF, pH = 9. Charge obtained by integration of voltammetry curves. Charge and reflectivity expressed relative to values at 0.000 V vs RHE. Optical conditions are the same as for Fig. 1.

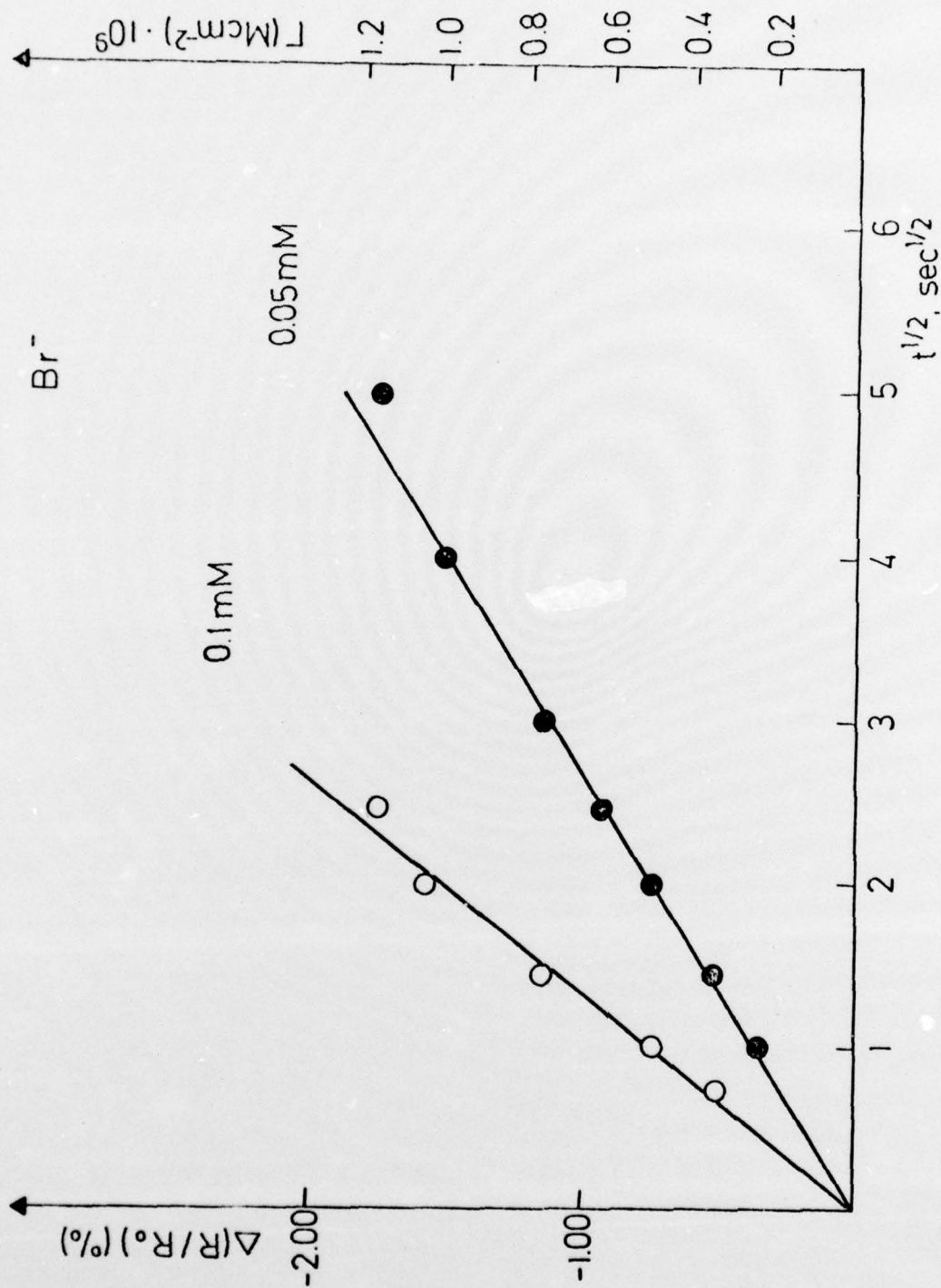


Fig. 3 Time dependence of the reflectivity change at 500 nm attending adsorption of Br⁻ on gold following a potential step from 0.2 V to 0.7 V vs RHE at various Br⁻ concentrations in 0.8 M NaF. The right ordinate is the calculated value of the surface excess of Br⁻.

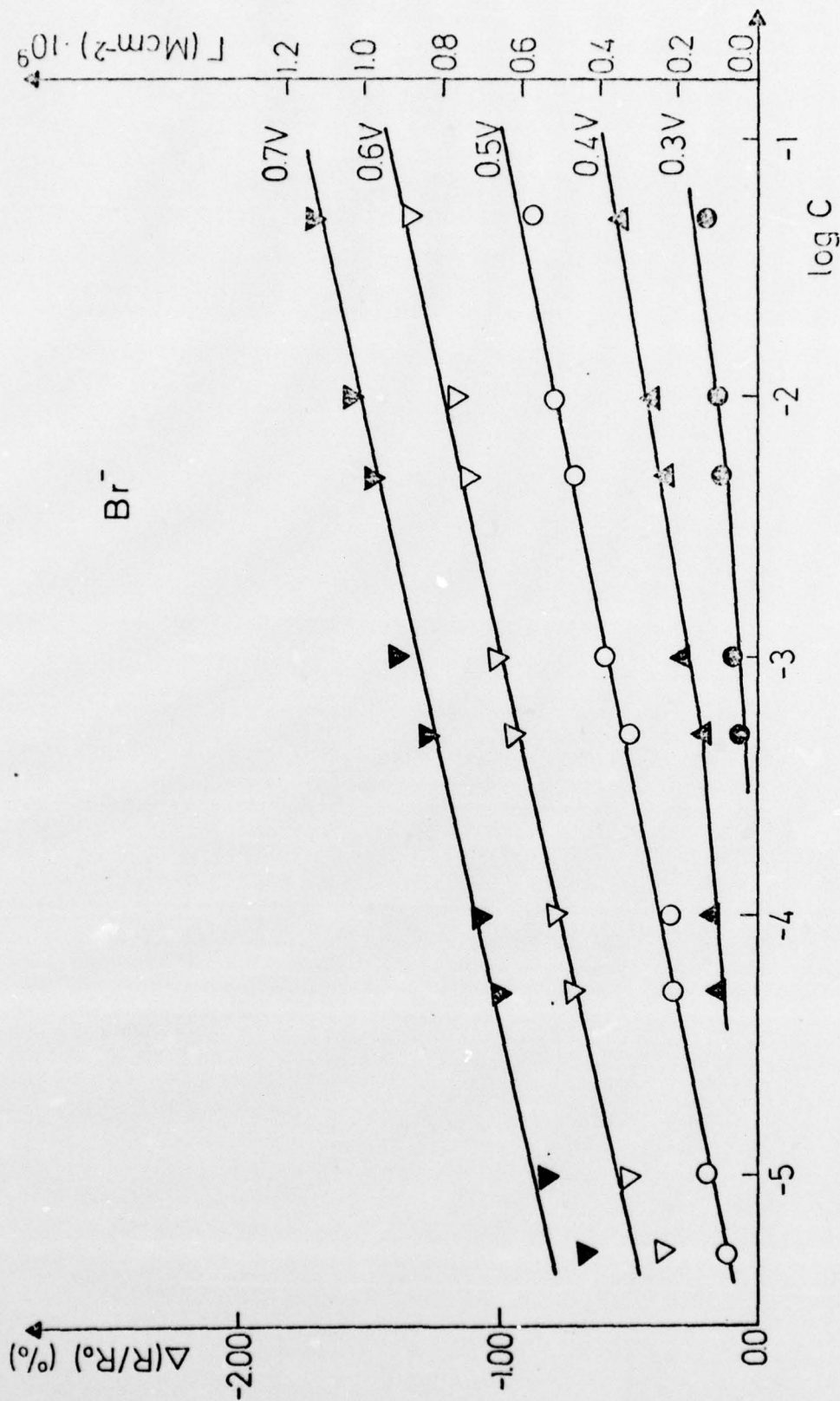


Fig. 4 Adsorption isotherms of Br^- on cold in 0.3 M NaF, pH = 9 evaluated from the curves in Fig. 1.

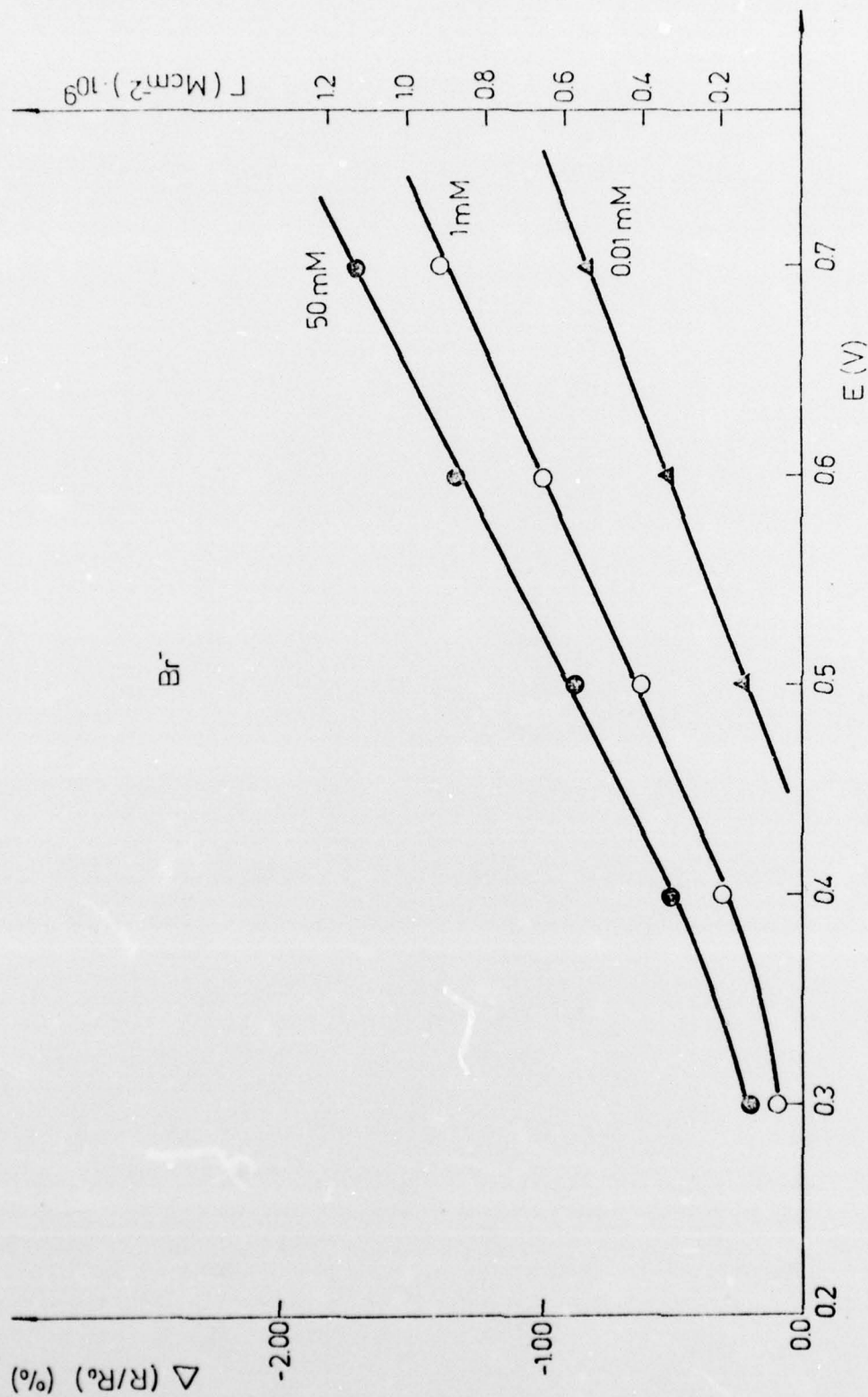


Fig. 5 Potential dependence of $\Delta R/R_0$ and Γ for several concentrations of Br⁻ which are indicated on the curves. These curves are obtained from those in Fig. 1.

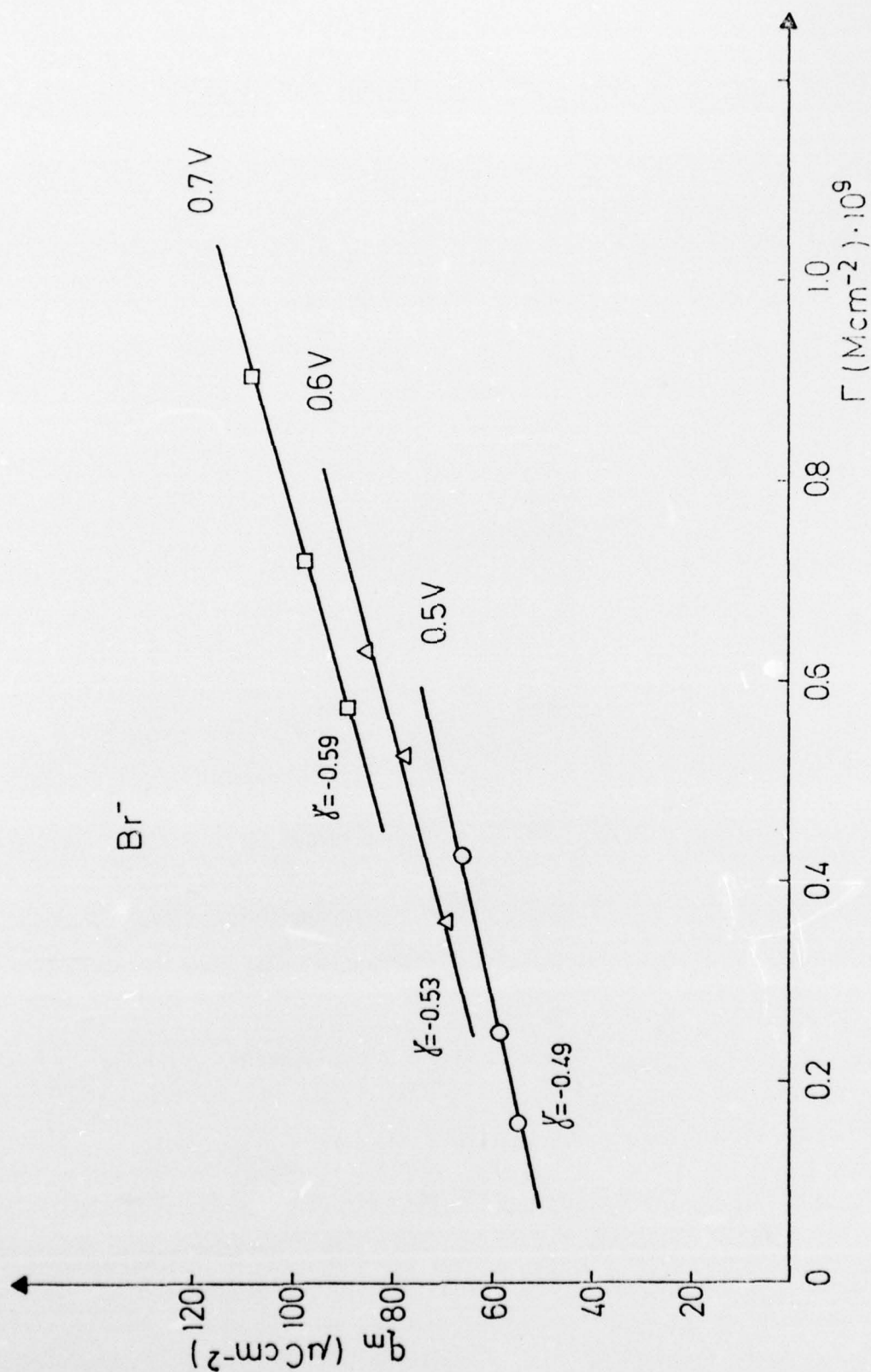


Fig. 6 Charge as a function of the surface excess Γ of Br⁻ adsorbed on gold for various electrode potentials. Data evaluated from reflectivity measurements and voltammetry curves. The electroabsorption valencies and electrode potentials are indicated on the curves.

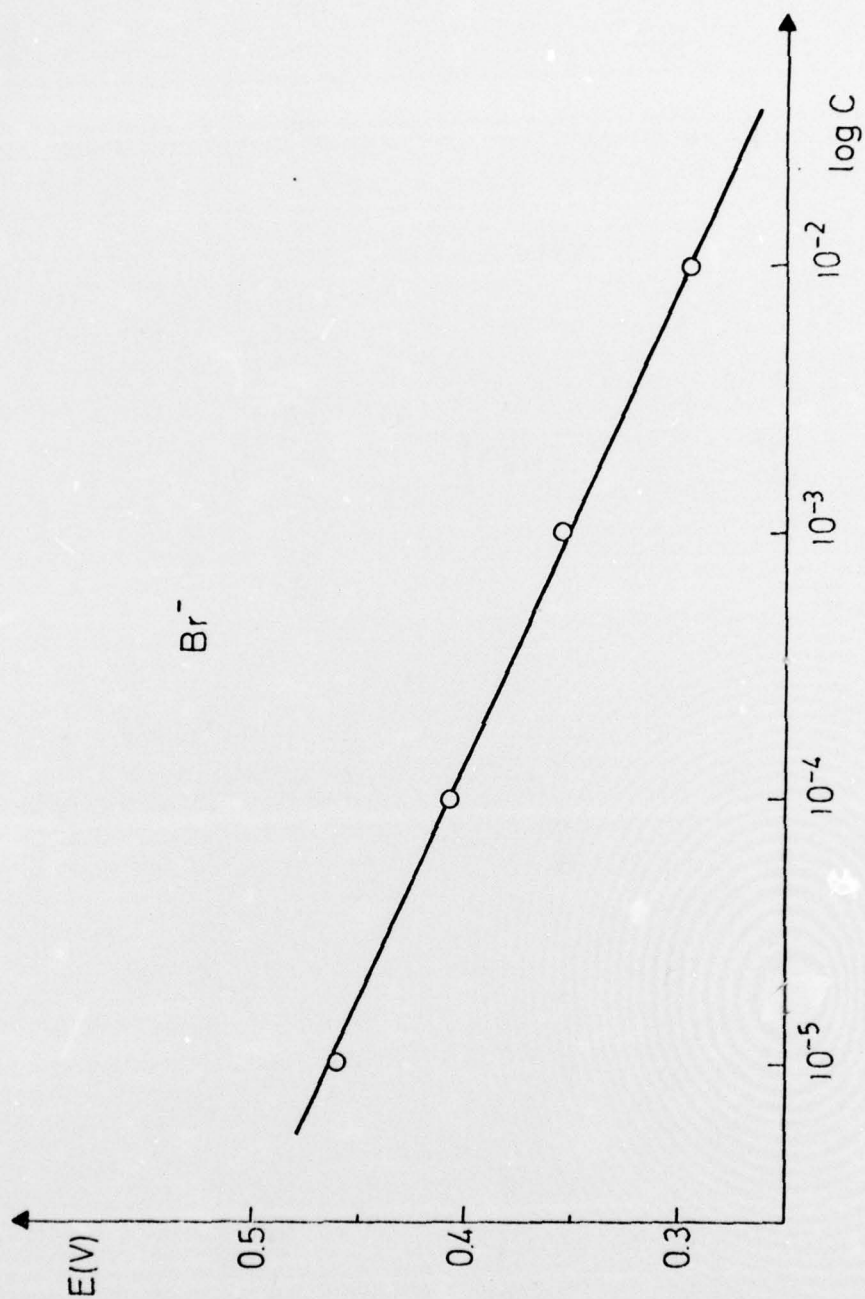


Fig. 7 Shift of potential of intersection of the two linear regions of reflectivity-potential curves in Fig. 1 as a function of Br^- concentration. Other conditions the same as for Fig. 1.

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